



# Air Resources Board



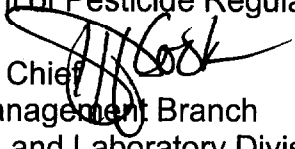
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TO: John Sanders, Ph.D., Chief  
Environmental Monitoring Branch  
Department of Pesticide Regulation

FROM: Jeff Cook, Chief   
Quality Management Branch  
Monitoring and Laboratory Division

DATE: January 3, 2005

SUBJECT: FINAL REPORT FOR THE 2003 APPLICATION AIR MONITORING FOR  
CHLOROPICRIN IN SANTA CRUZ COUNTY

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Attached is the final "Report for Air Monitoring Around a Bed Fumigation of Chloropicrin in Santa Cruz County – November 2003." Also attached is the separate volume of appendices for the report. We received your September 14, 2004, comments on the draft report and have made the recommended changes.

If you or your staff have questions or need further information, please contact me at (916) 322-3726 or via email at [jcook@arb.ca.gov](mailto:jcook@arb.ca.gov) or Webster Tasat at (916) 322-7055 or via email at [wtasat@arb.ca.gov](mailto:wtasat@arb.ca.gov).

## Attachment/Separate Appendices

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*The energy challenge facing California is real. Every Californian needs to take immediate action to reduce energy consumption. For a list of simple ways you can reduce demand and cut your energy costs, see our Website: <http://www.arb.ca.gov>.*

California Environmental Protection Agency

California Environmental Protection Agency

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 **Air Resources Board**

State of California  
California Environmental Protection Agency  
AIR RESOURCES BOARD

**Report on Air Monitoring  
Around a Bed Fumigation  
of Chloropicrin in Santa Cruz County  
November 2003**

Prepared by  
Operations Planning and Assessment Section  
Quality Management Branch  
Monitoring and Laboratory Division

Project No. P-03-001

December 1, 2004

This report has been reviewed by the staff of the California Air Resources Board and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Air Resources Board, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

## Monitoring Report Approval

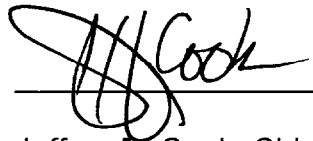
**Report Title:** Air Monitoring Around a Bed Fumigation of Chloropicrin - November 2003

**Project Lead:** Kevin Mongar, Air Pollution Specialist

**Prepared by:** Kathy Gill, Air Pollution Specialist and Kevin Mongar

**Approval:** The following monitoring report has been reviewed and approved by the Monitoring and Laboratory Division.

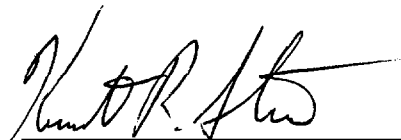
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Date



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## **Executive Summary**

### **Report on Air Monitoring Around a Bed Fumigation of Chloropicrin in Santa Cruz County - November 2003**

This report presents the results of application air monitoring for chloropicrin conducted in Santa Cruz County associated with a bed fumigation on a 4.8 acre field (pre-plant for strawberries) from November 12 to November 16, 2003. The field was fumigated with a 50:50 mixture of chloropicrin and methyl bromide. In addition to the ARB's chloropicrin monitoring, staff of the Department of Pesticide Regulation collected samples for methyl bromide, which were analyzed by The California Department of Food and Agriculture's Center for Analytical Chemistry-Environmental Monitoring Section. This report addresses only the monitoring for chloropicrin and not the DPR sampling/analysis for methyl bromide. The bar graph attached to this Executive Summary illustrates the results of the ARB's chloropicrin application study.

The monitoring included samples collected for two background periods (i.e., samples collected around the field prior to the test application) and six sampling periods during and after the single day application.

The application monitored during this study was conducted on November 13, 2003. Several other bed fumigation applications of chloropicrin and methyl bromide were conducted on adjacent plots several days prior to the start of the monitoring study. An application was made on plots directly to the east of the southeast portion of the test plot on November 8, 2003. The "southeast" (SE) sampler was located within the area that received the application on November 8, 2003. Another application was made on plots directly to the east/northeast of the test plot on November 10, 2003. The "northeast" (NE) and "east" (E) samplers were located within the area that received the application on November 10, 2003.

Background samples were collected from 0630 to 1700 (daytime) and 1700 to 0600 (nighttime) on November 12 to 13, 2003. Thus, the background sampling was conducted for approximately 24 hours just prior to the start of the application test (i.e., to document the levels of chloropicrin in the air at the test site just prior to the application being monitored). The background samples were collected at the northwest (NW), northeast (NE), southeast (SE), and southwest (SW) sites. All background sample results were above the estimated quantitation limit (EQL).

Forty-eight application samples were collected (spikes, blanks, background samples and the lower of each pair of collocated samples excluded). Four samples were invalidated due to flow rate deviations caused by rain or sampler malfunction. Of the 44 valid samples, 43 sample results were above the EQL, one sample result was below the EQL but "detected", and no sample results were less than the method detection limit (MDL).

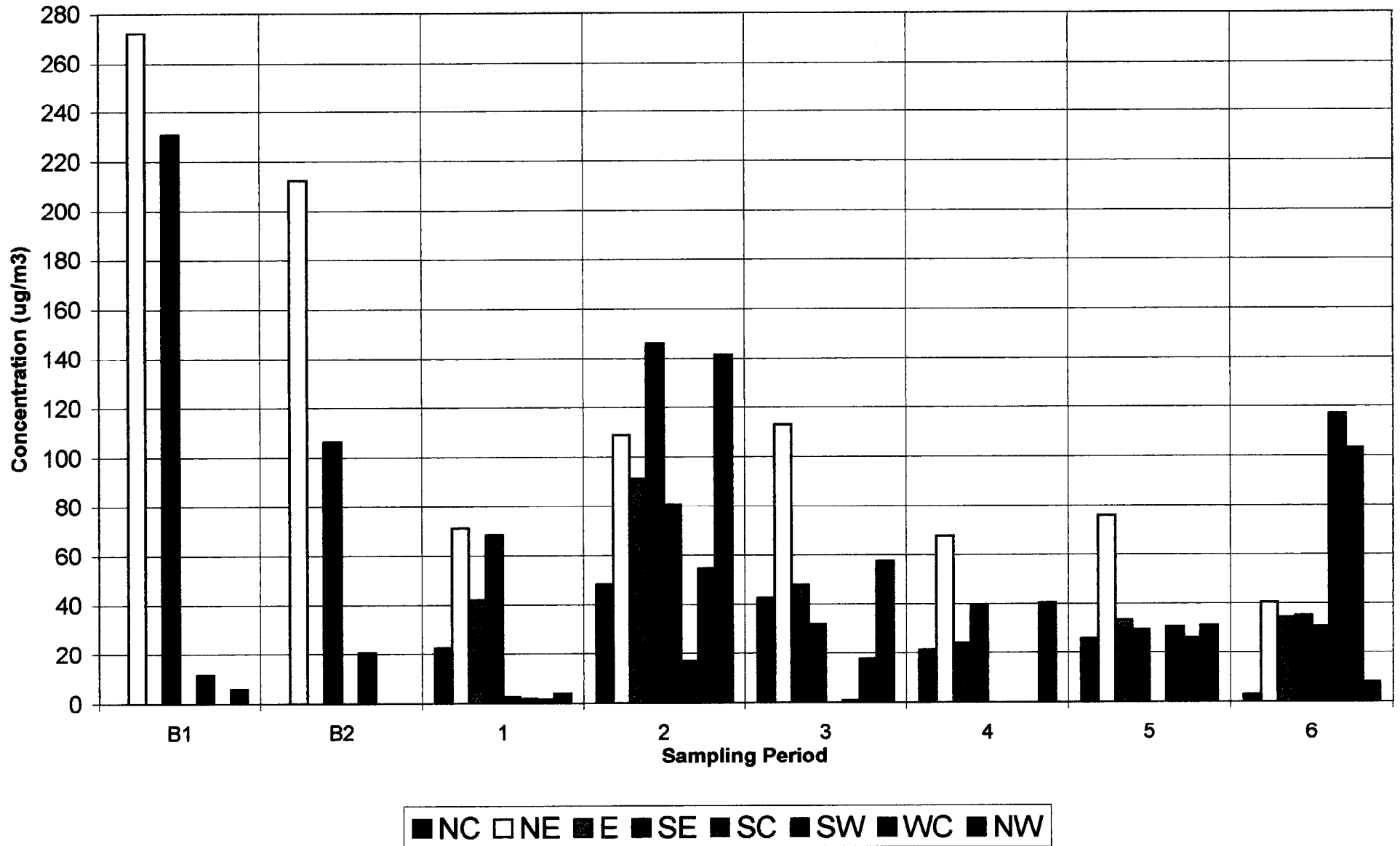
The highest concentration, 270  $\mu\text{g}/\text{m}^3$  (40.5 ppbv), was observed at the NE sampling site during the daytime background sampling period. The next highest concentration, 230  $\mu\text{g}/\text{m}^3$  (34.3 ppbv), was observed at the SE sampling site during the daytime

background sampling period. Again, the SE and NE samplers were located within the areas that received applications on November 8 and 10, 2003, respectively. The high chloropicrin levels observed during the background sampling was apparently due to residual chloropicrin from those previous applications.

The application test sample results (i.e., during and post application) ranged from “detected” to  $150 \text{ ug/m}^3$  (22 ppbv).

The results of this study should be used with caution due to the uncertainty of the origin of the chloropicrin. In other words, the levels of chloropicrin determined in the air during the study are likely due to contributions (off gassing) from both the test plot as well as adjacent or nearby prior applications. In addition, rain occurred during and following the application, further complicating the off gassing and interpretation of results.

## Chloropicrin Fumigation Monitoring Results



## **Acknowledgments**

Assistance in sampling site selection was provided by staff of the Santa Cruz County Agricultural Commissioner's Office. Staff of the ARB Air Quality Surveillance Branch (AQSB) collected the ambient samples. Steve Rider of the AQSB coordinated the field work. Michael Orbanosky of the ARB Special Analysis Section laboratory performed the chemical analyses. Lynn Baker of the ARB Stationary Source Division provided helpful advice and comments in regard to project planning and the monitoring protocol and report.

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# **DRAFT Report on Air Monitoring Around a Bed Fumigation of Chloropicrin in Santa Cruz County - November 2003**

## **I. Introduction**

At the request of the California Department of Pesticide Regulation (DPR) (October 18, 2002 Memorandum, Helliker to Lloyd), the Air Resources Board (ARB) staff determined airborne concentrations of the pesticide chloropicrin around a bed fumigation application. The study, conducted in Santa Cruz County, was associated with a bed fumigation on a 4.8 acre field (pre-plant for strawberries) from November 12 to November 16, 2003. This monitoring was done to fulfill the requirements of Assembly Bill 1807/3219 (Food and Agricultural Code, Division 7, Chapter 3, Article 1.5) which requires the ARB "to document the level of airborne emissions...of pesticides which may be determined to pose a present or potential hazard..." when requested by the DPR. The DPR requested that a chloropicrin application be selected for the monitoring study where methyl bromide was also being used. The DPR collected samples for methyl bromide at the same time ARB collected samples for chloropicrin. The California Department of Food and Agriculture's Center for Analytical Chemistry-Environmental Monitoring Section analyzed the DPR samples. This report addresses only the monitoring for chloropicrin and not the DPR sampling/analysis for methyl bromide.

The sampling and analysis followed the procedures outlined in 1) the monitoring protocol (Appendix 1 of the separate volume of Appendices), 2) the quality assurance guidelines described in the "Quality Assurance Plan for Pesticide Air Monitoring" (May 11, 1999 version) (page 10 of the Appendices), and 3) the procedures described in the "Standard Operating Procedure, Sampling and Analysis of Trichloronitromethane (Chloropicrin) in Application and Ambient Air using Gas Chromatography/Mass Selective Detector" (Appendix VII).

## **II. Sampling**

Chloropicrin samples were collected on XAD-4 resin sampling cartridges. The cartridges were 8 mm x 140 mm, XAD-4, with 400 mg of resin in the primary section, and 200 mg in the secondary section (obtained from SKC special order). Sample collection was at a flow rate of 100 standard cubic centimeters per minute (sccpm). Subsequent to sampling, the cartridges were capped, labeled, placed in a culture tube, and stored and transported in an insulated container with dry ice. The samples were driven to the ARB laboratory in Sacramento for analysis. Caution was used during field monitoring, transportation, storage, and lab analysis to minimize exposure of samples to sunlight in order to prevent photo degradation of chloropicrin.

Each sampler consisted of an adsorbent cartridge, Teflon fittings and tubing, rain/sun shield, needle valve, support, and a 12 volt DC vacuum pump (see Appendix I page 9). Each cartridge was prepared in the field by breaking off both sealed glass ends and then immediately inserting the cartridge into the fitting. The cartridges were oriented in

the sampler with the small arrow printed on the side of each cartridge indicating the direction of flow. Needle valves were used to control the flow for sampling. The flow rates were set using a calibrated digital mass flow meter (MFM) before the start of each sampling period. The MFM used for the chloropicrin samplers has a range of 0-200 sccpm. The mass flow meter was calibrated to standard conditions (1 atm and 25 °C). The flow rate was also checked and recorded, using the MFM, at the end of each sampling period. Any change in flow rates was recorded on the field log sheets (page 98 of the Appendices). The pesticide sampling procedures for adsorbent cartridges are included on page 46 of the Appendices.

### III. Application Monitoring

The DPR's monitoring recommendation (July 25, 2001 memo, Sanders to Cook, Updated Monitoring Recommendations for 2001) suggested that application-site air monitoring should be conducted around a bed fumigation of chloropicrin in which methyl bromide was also used so that they could be monitored simultaneously. Ideally, monitoring was to be conducted at a site using the highest allowed rates of use of chloropicrin (i.e., between 150 to 400 pounds per acre overall). The sampling schedule recommended by the DPR consisted of samples collected during daylight and overnight periods as shown below in Table 1.

**Table 1 Application Sampling Schedule**

<b>Sample period begins</b>	<b>Sample duration time</b>
Background (pre-application)	Two sequential 12-hour samples (daytime/overnight)
During application and post – application	Start of application until 1 hour before sunset (or until end of application if after sunset)
1 hour before sunset	Overnight (until 1 hour after sunrise)
1 hour after sunrise	Daytime (until 1 hour before sunset)
1 hour before sunset	Overnight (until 1 hour after sunrise)
1 hour after sunrise	Daytime (until 1 hour before sunset)
1 hour before sunset	Overnight (until 1 hour after sunrise)

A field of approximately 4.8 acres in Santa Cruz County was chosen for the application monitoring site. Refer to Figure 1 for a diagram of the application site and surrounding area. Refer to Appendix III (page 74 of Appendices) for a copy of the Notice of Intent to Apply Restricted Materials. Table 2 summarizes the site specific application information.

**Table 2      Application Information**

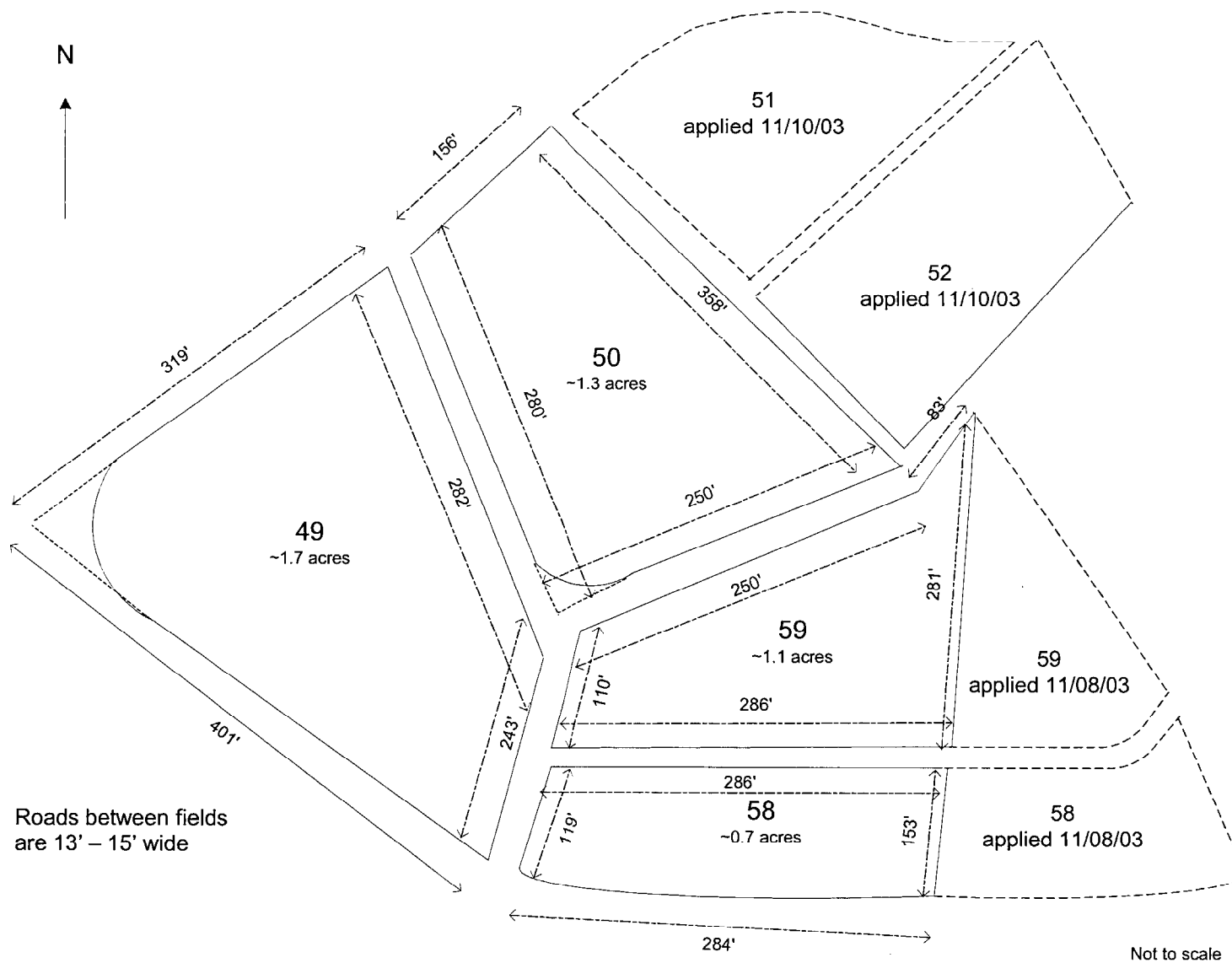
<b>Location</b>	Watsonville, CA, East of San Andreas Road, Santa Cruz County
<b>R/T/S</b>	1E/12S/14
<b>Field Size</b>	Approximately 4.8 acres
<b>Product Applied</b>	Tri-Con; 50% methyl bromide, 50% chloropicrin (by weight)
<b>Type of Application</b>	Bed tarpaulin fumigation, black tarp, 1.5 mil thickness
<b>Commodity</b>	Soil, strawberry pre-plant
<b>Application Rate</b>	300 lbs. Tricon per acre
<b>Grower/Applicator</b>	Jertberg Farm

The samplers were located approximately 160 ( $\pm$  5) feet from the edge of the field at the inner buffer zone distance. Refer to Figure 2 for a diagram of the location of the samplers around the application site. Eight samplers were positioned around the field. A ninth sampler was collocated at the NE (northeast) position. Table 3 lists the GPS coordinates of the sampler locations. Due to the furrow heights and hilly conditions, sampler inlets were approximately 3.6 to 4.5 feet above the bed level. All samplers were at the same elevation relative to the field. There were no obstacles obstructing the air flow between the field and the samplers.

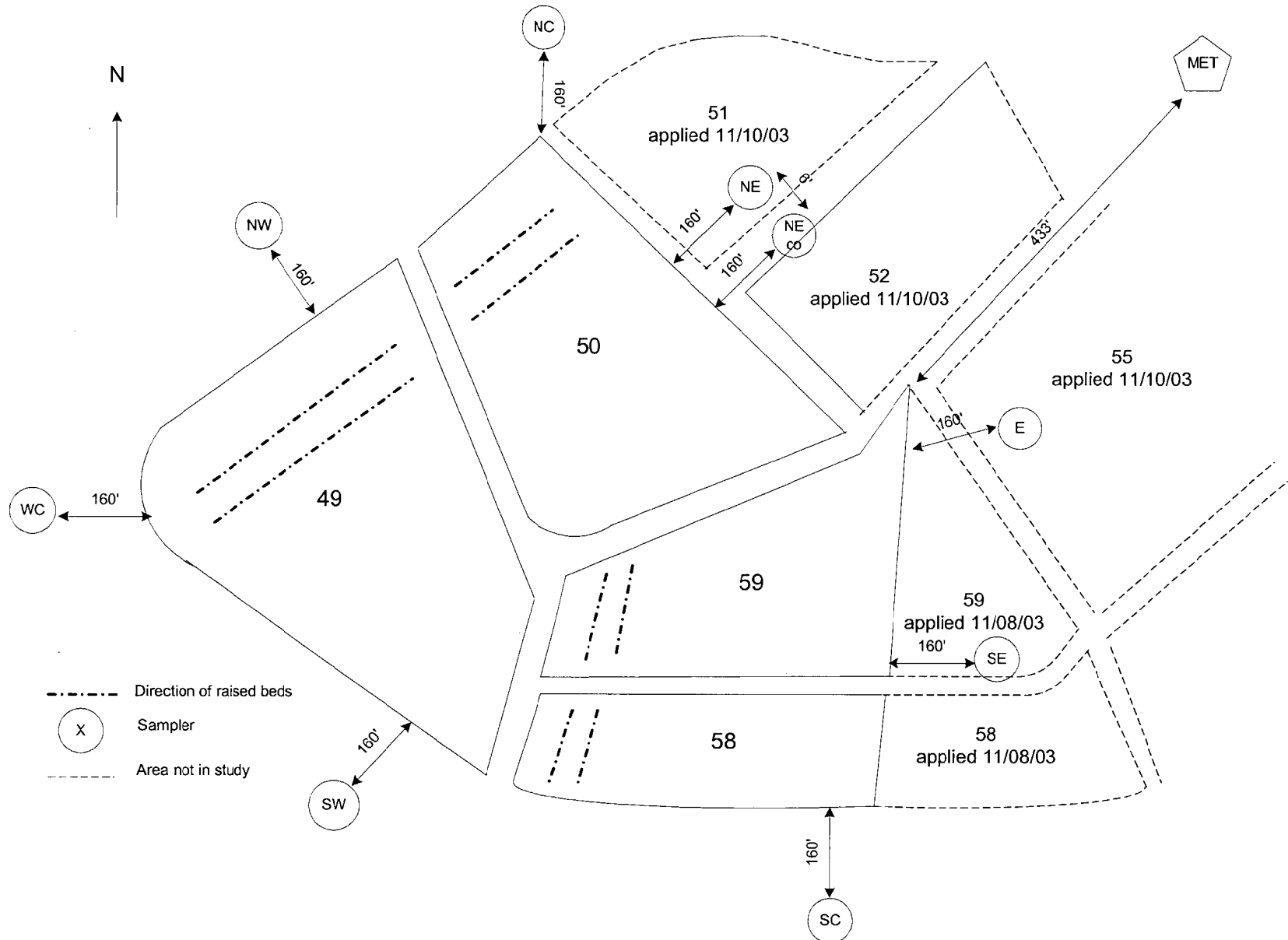
**Table 3      Sampler Waypoints**

<b>Sampler ID</b>	<b>Sampler Position</b>	<b>Waypoints</b>
MET (Meteorological Station)	East Northeast	N 36° 39.222', W 121° 34.762'
SE	Southeast Side	N 36° 53.059', W 121° 49.159'
SW	Southwest Side	N 36° 53.033', W 121° 49.297'
NE	Northeast Side	N 36° 53.138', W 121° 49.199'
NW	Northwest Side	N 36° 53.134', W 121° 49.308'
WC	West Corner	N 36° 53.075', W 121° 49.342'
E	East Corner	N 36° 53.112', W 121° 49.151'
NC	North Corner	N 36° 53.170', W 121° 49.244'
SC	South Corner	N 36° 53.008', W 121° 49.218'

Figure 1 Application Site



**Figure 2     Sampler Locations**



The monitoring included samples collected for two background periods (i.e., samples collected around the field prior to the test application) and six sampling periods during and after the single day application.

The application monitored during this study was conducted on November 13, 2003. Several other bed fumigation applications of chloropicrin and methyl bromide were conducted on adjacent plots several days prior to the start of the monitoring study. An application was made on plots directly to the east of the southeast portion of the test plot on November 8, 2003. The "southeast" (SE) sampler was located within the area that received the application on November 8, 2003. Another application was made on plots directly to the east/northeast of the test plot on November 10, 2003. The "northeast" (NE) and "east" (E) samplers were located within the area that received the application on November 10, 2003.

Background samples were collected from 0630 to 1700 (daytime) and 1700 to 0600 (nighttime) on November 12 to 13, 2003. Thus, the background sampling was conducted for approximately 24 hours just prior to the start of the application test (i.e., to document the levels of chloropicrin in the air at the test site just prior to the application being monitored). The background samples were collected at the northwest (NW), northeast (NE), southeast (SE), and southwest (SW) sites. Field spike samples were collected (collocated) during the daytime background sampling.

The application procedure was conducted by tractor (shank injection followed by tarp) and started in fields 58 and 59 working in a north-northeast to south-southwest manner. Fields 49 and 50 were treated as one field and application proceeded from east-northeast to west-southwest. See Figure 2 for field designations and the application directions, which were the same as the directions of the raised beds on each field. Table 4 lists the approximate sampling periods. The length of time required to make the circuit and change all of the samples for each change-out was about 50 minutes.

**Table 4      Application Sampling Periods**

<b>Sampling Period</b>	<b>Approx. Sampling Duration (Hours)</b>	<b>Date</b>	<b>Time</b>
Background 1 (Daytime)	10 1/2	11/12/03	0630 to 1700
Background 2 (Overnight)	13	11/12-13/03	1700 to 0600
1 (Application)	8 1/2	11/13/03	0730 to 1600
2 (Overnight)	16	11/13-14/03	1600 to 0800
3 (Daytime)	8 1/2	11/14/03	0800 to 1630
4 (Overnight)	16	11/14-15/03	1600 to 0800
5 (Daytime)	8 1/2	11/15/03	0730 to 1600
6 (Overnight)	16	11/15-16/03	1600 to 0800

The meteorological station (oriented toward true north) was positioned  $433 \pm 5$  feet to the east-northeast of the field. The meteorological station was positioned, at a height of 21 feet, to determine wind speed and direction, air temperature, barometric pressure

and relative humidity. The raw meteorological station data is available in comma delimited text format. Appendix IV (page 78 of the Appendices) lists the meteorological station data in 15-minute averages for the test period.

Weather conditions were reported in the field notes as follows. "November 11<sup>th</sup> through the 13<sup>th</sup> were sunny with a bit of fog and a mean temperature of approximately 13°C and a mean wind speed of 5 mph. The 14<sup>th</sup> started out sunny, but progressively got cloudier and finally started drizzling hard while SPM performed the evening sample recovery. A total of 0.05" was measured at the official Watsonville weather site for the 14<sup>th</sup>. The 15<sup>th</sup> was overcast and rainy all day until late afternoon. The 15<sup>th</sup> had a mean temperature of 11°C and a mean wind speed of 2.5 mph. A total of 0.24" of rain dropped from 0000 till the late afternoon on the 15<sup>th</sup>. The 16<sup>th</sup> started with a bit of fog, but turned sunny through the shutdown of air monitoring."

#### **IV. Analytical Methodology**

The sampling and analysis method and validation results for chloropicrin are included in the laboratory report (page 63 of the Appendices). The chloropicrin method consists of sampling with XAD-4 resin cartridges and analysis using gas chromatography with mass selective detector. The method detection limit (MDL) and estimated quantitation limit (EQL) for chloropicrin were determined by analyzing 7 spiked replicates as per 40CFR Part 136 Appendix B. MDL and EQL were set by the lab staff at 3.96 nanograms per sample (ng/sample) and 19.80 ng/sample, respectively. Based on 0.144 cubic meters (m<sup>3</sup>) of air collected the method EQL achieved was 0.14 ug/m<sup>3</sup>, for a 24-hour period. DPR had requested an EQL of 0.1 ug/m<sup>3</sup>.

Results equal to or above the MDL but below the EQL were reported as detected (Det). Laboratory results, in units of ug/sample, equal to or above the EQL were reported to 3 significant figures. The laboratory results are included in Appendix II. The ARB Northern Laboratory Branch laboratory in Sacramento performed the analyses.

#### **V. Application Monitoring Results**

Table 5 presents the results of application air monitoring for chloropicrin in units of ug/m<sup>3</sup> and parts per billion by volume (ppbv). A summary of the results is presented in Table 6 (and in the Figure in the Executive Summary). The equation used to convert chloropicrin air concentration results from units of ug/m<sup>3</sup> to units of ppbv at 1 atmosphere and 25 °C is shown below.

$$\text{ppbv} = (\text{ug/m}^3) \times \frac{(0.0820575 \text{ liter-atm/mole-}^\circ\text{K})(298^\circ\text{K})}{(1 \text{ atm})(164.4 \text{ gram/mole})} = (0.1487) \times (\text{ug/m}^3)$$

Four samples were collected for each of the two background periods (i.e., daytime and overnight prior to application) from the northeast (NE), northwest (NW), southeast (SE) and southwest (SW) sites. During both background sampling periods, all of the sample results were above the EQL. The highest concentration detected during the study was 270 ug/m<sup>3</sup> found at the northeast site during the daytime Background period.

Of the forty-eight (48) application samples collected (spikes, blanks, background samples and the lower of each pair of collocated samples excluded) 42 sample results were found to be above the EQL, one sample result was “detected”, no sample results were <MDL, and five samples were invalidated due flow rate deviations caused by rain or a sampling problem.

Samples were labelled using the following format:

Sampler ID – C (for compound monitored – chloropicrin) – Sample Period

If a collocated sample was collected, there will be an additional “C” after the Sample Period. See Table 3 for Sampler IDs and Table 4 for Sample Periods.

No sample results have been adjusted or corrected for recoveries of quality assurance spike samples.

Wind speed and direction have been plotted on wind rose diagrams for each of the sampling periods and are shown in Figures 3 through 10. Sample results for each sampling site and for each period are included on the wind roses positioned with correct directional orientation and percent time at each direction relative to the field. Further descriptive information on individual wind roses is included in the figures in Appendix IV.

The results of this study should be used with caution due to the uncertainty of the origin of the chloropicrin. In other words, the levels of chloropicrin determined in the air during the study are likely due to contributions (off gassing) from both the test plot as well as adjacent or nearby prior applications. In addition, rain occurred during and following the application, further complicating the off gassing and interpretation of results.

**Table 5 Chloropicrin Application Monitoring Results**

Log #	Sample ID	Start Date/Time	End Date/Time	Time (hours)	Volume (m3)	Chloropicrin			Data Flags
						(ug/sample)	(ug/m3)	(ppbv)	
1	SE-C-B1	11/12/03 0850	11/12/03 1648	8.0	0.048	1.10E+01	2.3E+02	3.4E+01	
3	SW-C-B1	11/12/03 0631	11/12/03 1659	10.5	0.063	7.31E-01	1.2E+01	1.7E+00	
5	NW-C-B1	11/12/03 0639	11/12/03 1710	10.5	0.067	3.91E-01	5.8E+00	8.6E-01	2
7	NE-C-B1	11/12/03 0647	11/12/03 1722	10.6	0.064	1.73E+01	2.7E+02	4.1E+01	
11	SE-C-B2	11/12/03 1652	11/13/03 0553	13.0	0.078	8.30E+00	1.1E+02	1.6E+01	
12	SW-C-B2	11/12/03 1702	11/13/03 0611	13.2	0.079	1.63E+00	2.1E+01	3.1E+00	
13	NW-C-B2	11/12/03 1714	11/13/03 0624	13.2	0.079	NA	NA	NA	1
14	NE-C-B2	11/12/03 1726	11/13/03 0634	13.1	0.079	1.67E+01	2.1E+02	3.2E+01	
15	E-C-1	11/13/03 0741	11/13/03 1636	8.9	0.053	2.24E+00	4.2E+01	6.2E+00	
16	SE-C-1	11/13/03 0724	11/13/03 1552	8.5	0.051	3.48E+00	6.9E+01	1.0E+01	
17	SC-C-1	11/13/03 0727	11/13/03 1600	8.5	0.051	1.31E-01	2.6E+00	3.8E-01	
18	SW-C-1	11/13/03 0730	11/13/03 1605	8.6	0.052	8.87E-02	1.7E+00	2.6E-01	
19	WC-C-1	11/13/03 0732	11/13/03 1610	8.6	0.052	8.11E-02	1.6E+00	2.3E-01	
20	NW-C-1	11/13/03 0734	11/13/03 1615	8.7	0.052	1.96E-01	3.8E+00	5.6E-01	
21	NC-C-1	11/13/03 0736	11/13/03 1620	8.7	0.052	1.18E+00	2.3E+01	3.4E+00	
22	NE-C-1	11/13/03 0738	11/13/03 1629	8.8	0.053	3.79E+00	7.1E+01	1.1E+01	
23	NE-C-1C	11/13/03 0738	11/13/03 1626	8.8	0.053	3.61E+00	6.8E+01	1.0E+01	
24	SE-C-2	11/13/03 1554	11/14/03 0734	15.7	0.094	1.37E+01	1.5E+02	2.2E+01	
25	SC-C-2	11/13/03 1601	11/14/03 0741	15.7	0.094	7.59E+00	8.1E+01	1.2E+01	
26	SW-C-2	11/13/03 1606	11/14/03 0746	15.7	0.094	1.59E+00	1.7E+01	2.5E+00	
27	WC-C-2	11/13/03 1611	11/14/03 0750	15.7	0.094	5.13E+00	5.5E+01	8.1E+00	
28	NW-C-2	11/13/03 1616	11/14/03 0756	15.7	0.094	1.33E+01	1.4E+02	2.1E+01	
29	NC-C-2	11/13/03 1621	11/14/03 0801	15.7	0.094	4.50E+00	4.8E+01	7.1E+00	
30	NE-C-2	11/13/03 1630	11/14/03 0809	15.7	0.094	1.02E+01	1.1E+02	1.6E+01	
31	NE-C-2C	11/13/03 1630	11/14/03 0807	15.6	0.094	8.84E+00	9.4E+01	1.4E+01	
32	E-C-2	11/13/03 1637	11/14/03 0813	15.6	0.094	8.52E+00	9.1E+01	1.4E+01	
33	SE-C-3	11/14/03 0735	11/14/03 1555	8.3	0.050	1.58E+00	3.2E+01	4.7E+00	
34	SC-C-3	11/14/03 0742	11/14/03 1602	8.3	0.050	Det	Det	Det	

MDL = 3.96ng/sample  
EQL = 19.80 ng/sample  
ppbv at 25° C and 1 atm

**Table 5 (cont.) Chloropicrin Application Monitoring Results**

Log #	Sample ID	Start Date/Time	End Date/Time	Time (hours)	Volume (m3)	Chloropicrin			Data Flags
						(ug/sample)	(ug/m3)	(ppbv)	
35	SW-C-3	11/14/03 0746	11/14/03 1608	8.4	0.050	4.36E-02	8.7E-01	1.3E-01	
36	WC-C-3	11/14/03 0751	11/14/03 1617	8.4	0.051	8.90E-01	1.8E+01	2.6E+00	3
37	NW-C-3	11/14/03 0757	11/14/03 1623	8.4	0.051	2.91E+00	5.7E+01	8.5E+00	3
38	NC-C-3	11/14/03 0802	11/14/03 1631	8.5	0.051	2.16E+00	4.2E+01	6.3E+00	3
39	NE-C-3	11/14/03 0809	11/14/03 1638	8.5	0.051	5.76E+00	1.1E+02	1.7E+01	3
40	NE-C-3C	11/14/03 0808	11/14/03 1632	8.4	0.050	5.45E+00	1.1E+02	1.6E+01	3
41	E-C-3	11/14/03 0815	11/14/03 1644	8.5	0.051	2.42E+00	4.8E+01	7.1E+00	3
42	SE-C-4	11/14/03 1556	11/15/03 0732	15.6	0.094	3.69E+00	3.9E+01	5.9E+00	
43	SC-C-4	11/14/03 1556	11/15/03 0732	15.6	NA	NA	NA	NA	1
44	SW-C-4	11/14/03 1556	11/15/03 0732	15.6	NA	NA	NA	NA	1
45	WC-C-4	11/14/03 1556	11/15/03 0732	15.6	NA	NA	NA	NA	1
46	NW-C-4	11/14/03 1556	11/15/03 0732	15.6	0.094	3.79E+00	4.1E+01	6.0E+00	3
47	NC-C-4	11/14/03 1556	11/15/03 0732	15.6	0.094	2.01E+00	2.1E+01	3.2E+00	3
48	NE-C-4	11/14/03 1556	11/15/03 0732	15.6	0.094	6.35E+00	6.8E+01	1.0E+01	3
49	NE-C-4C	11/14/03 1556	11/15/03 0732	15.6	0.094	5.23E+00	5.6E+01	8.3E+00	3
50	E-C-4	11/14/03 1556	11/15/03 0732	15.6	0.094	2.26E+00	2.4E+01	3.6E+00	3
51	SE-C-5	11/15/03 0733	11/15/03 1548	8.3	0.050	1.44E+00	2.9E+01	4.3E+00	
52	SC-C-5	11/15/03 0739	11/15/03 1554	8.3	NA	NA	NA	NA	1
53	SW-C-5	11/15/03 0746	11/15/03 1600	8.2	0.049	1.49E+00	3.0E+01	4.5E+00	
54	WC-C-5	11/15/03 0750	11/15/03 1657	9.1	0.055	1.42E+00	2.6E+01	3.9E+00	
55	NW-C-5	11/15/03 0756	11/15/03 1611	8.3	0.050	1.54E+00	3.1E+01	4.6E+00	
56	NC-C-5	11/15/03 0801	11/15/03 1616	8.3	0.050	1.28E+00	2.6E+01	3.8E+00	
57	NE-C-5	11/15/03 0811	11/15/03 1624	8.2	0.049	3.74E+00	7.6E+01	1.1E+01	
58	NE-C-5C	11/15/03 0808	11/15/03 1622	8.2	0.049	3.57E+00	7.2E+01	1.1E+01	
59	E-C-5	11/15/03 0817	11/15/03 1628	8.2	0.049	1.63E+00	3.3E+01	4.9E+00	
60	SE-C-6	11/15/03 1549	11/16/03 0731	15.7	0.094	3.29E+00	3.5E+01	5.2E+00	
61	SC-C-6	11/15/03 1556	11/16/03 0737	15.7	0.088	2.65E+00	3.0E+01	4.5E+00	2
62	SW-C-6	11/15/03 1601	11/16/03 0742	15.7	0.094	1.10E+01	1.2E+02	1.7E+01	

MDL = 3.96ng/sample  
EQL = 19.80 ng/sample  
ppbv at 25° C and 1 atm

**Table 5 (cont.) Chloropicrin Application Monitoring Results**

Log #	Sample ID	Start Date/Time	End Date/Time	Time (hours)	Volume (m3)	Chloropicrin			Data Flags
						(ug/sample)	(ug/m3)	(ppbv)	
63	WC-C-6	11/15/03 1608	11/16/03 0746	15.6	0.094	9.67E+00	1.0E+02	1.5E+01	
64	NW-C-6	11/15/03 1612	11/16/03 0751	15.6	0.094	7.51E-01	8.0E+00	1.2E+00	
65	NC-C-6	11/15/03 1617	11/16/03 0755	15.6	0.094	2.70E-01	2.9E+00	4.3E-01	
66	NE-C-6	11/15/03 1625	11/16/03 0801	15.6	0.094	3.79E+00	4.1E+01	6.0E+00	
67	NE-C-6C	11/15/03 1623	11/16/03 0800	15.6	0.094	3.58E+00	3.8E+01	5.7E+00	
68	E-C-6	11/15/03 1629	11/16/03 0806	15.6	0.094	3.21E+00	3.4E+01	5.1E+00	

1. Invalid sample due to field sampling problem; end flow rate > 25% different from the start rate
2. End flow rates were > 10% different from the start rate, start and end flow rates were averaged to determine volume
3. Mass flow meter not functional at either start or end of sampling period; flow rate not confirmed

Figure 4  
Background Period 1 11/12/03 Daytime Chloropicrin (ug/m3)



Values in **bold** adjacent to  
samplers are chloropicrin  
concentrations (ug/m3)

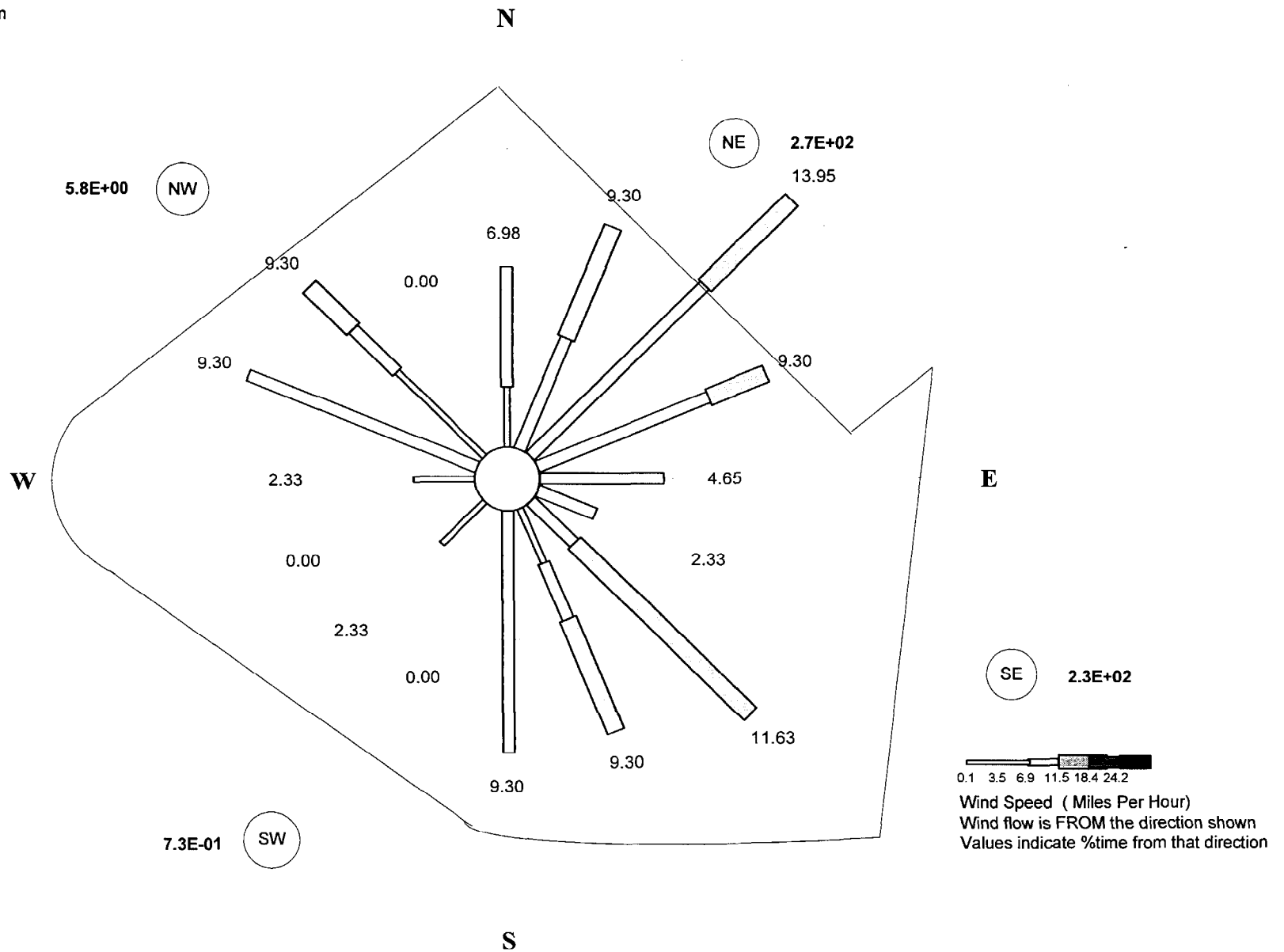


Figure 5  
Background Period 2 11/12/03 Overnight Chloropicrin (ug/m3)



Values in **bold** adjacent to samplers are chloropicrin concentrations (ug/m3)

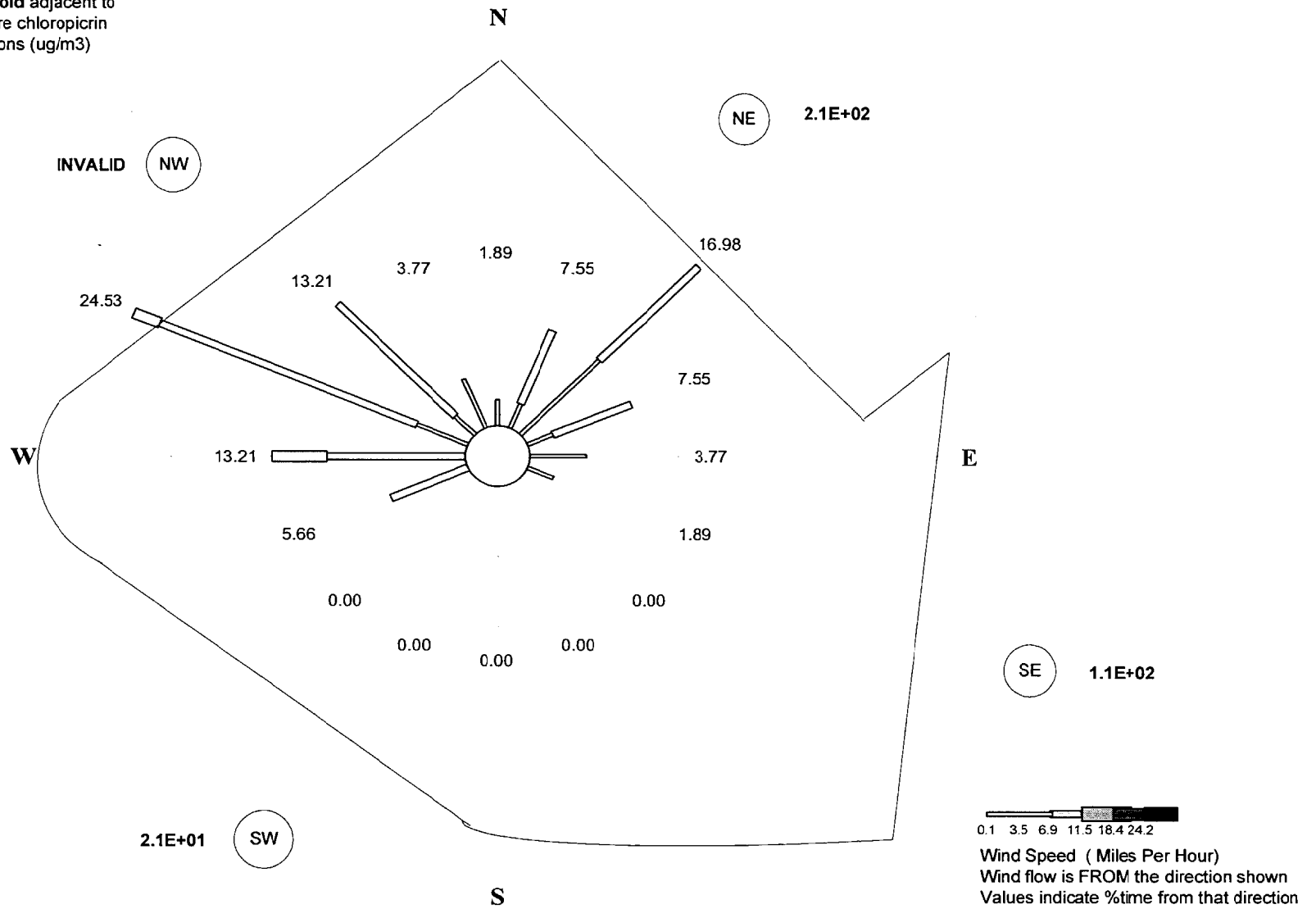
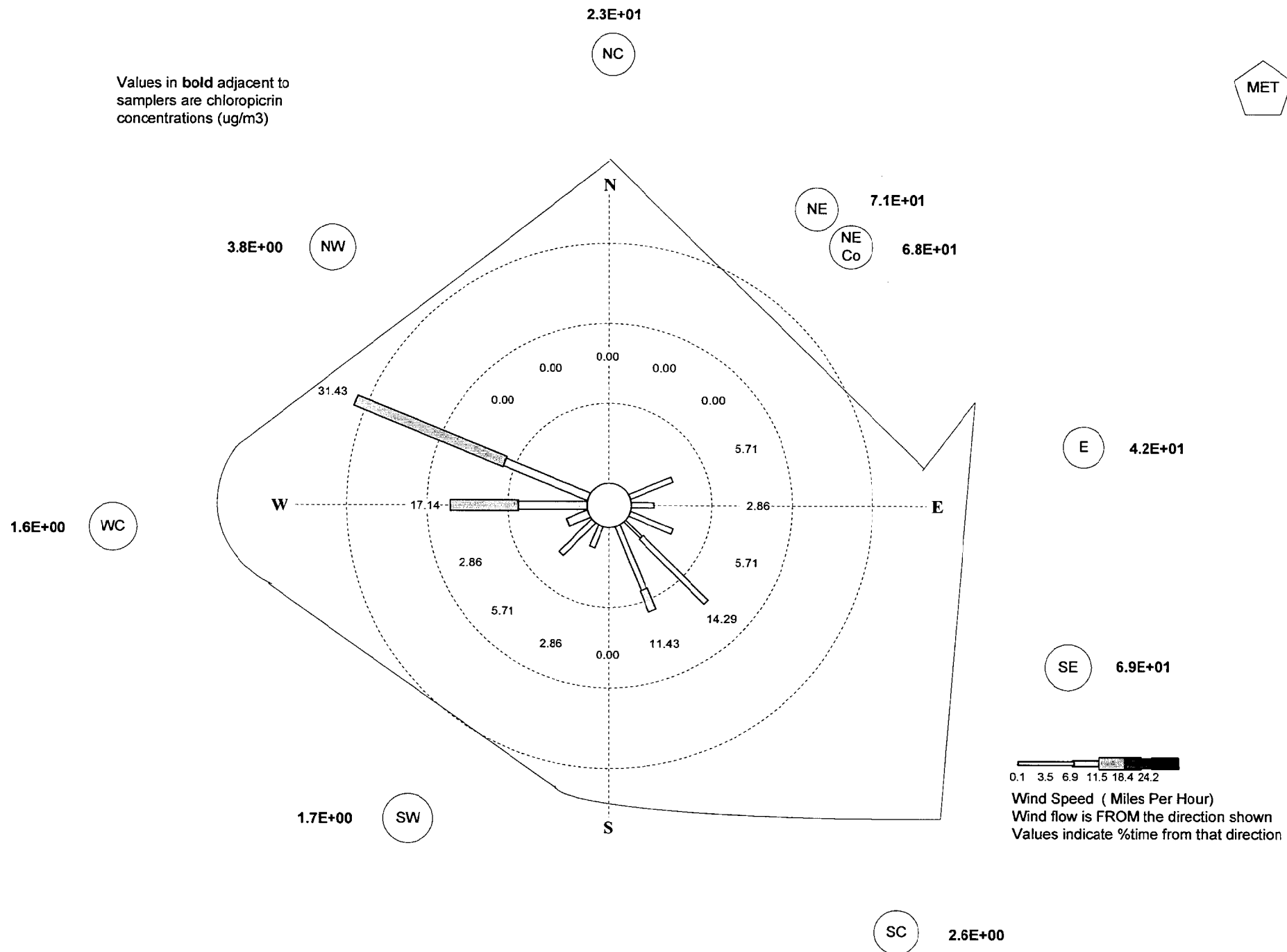


Figure 6  
Period 1 11/13/03 Daytime Chloropicrin (ug/m3)



**4.8E+01**



Figure 8  
Period 3 11/14/03 Daytime Chloropicrin (ug/m3)

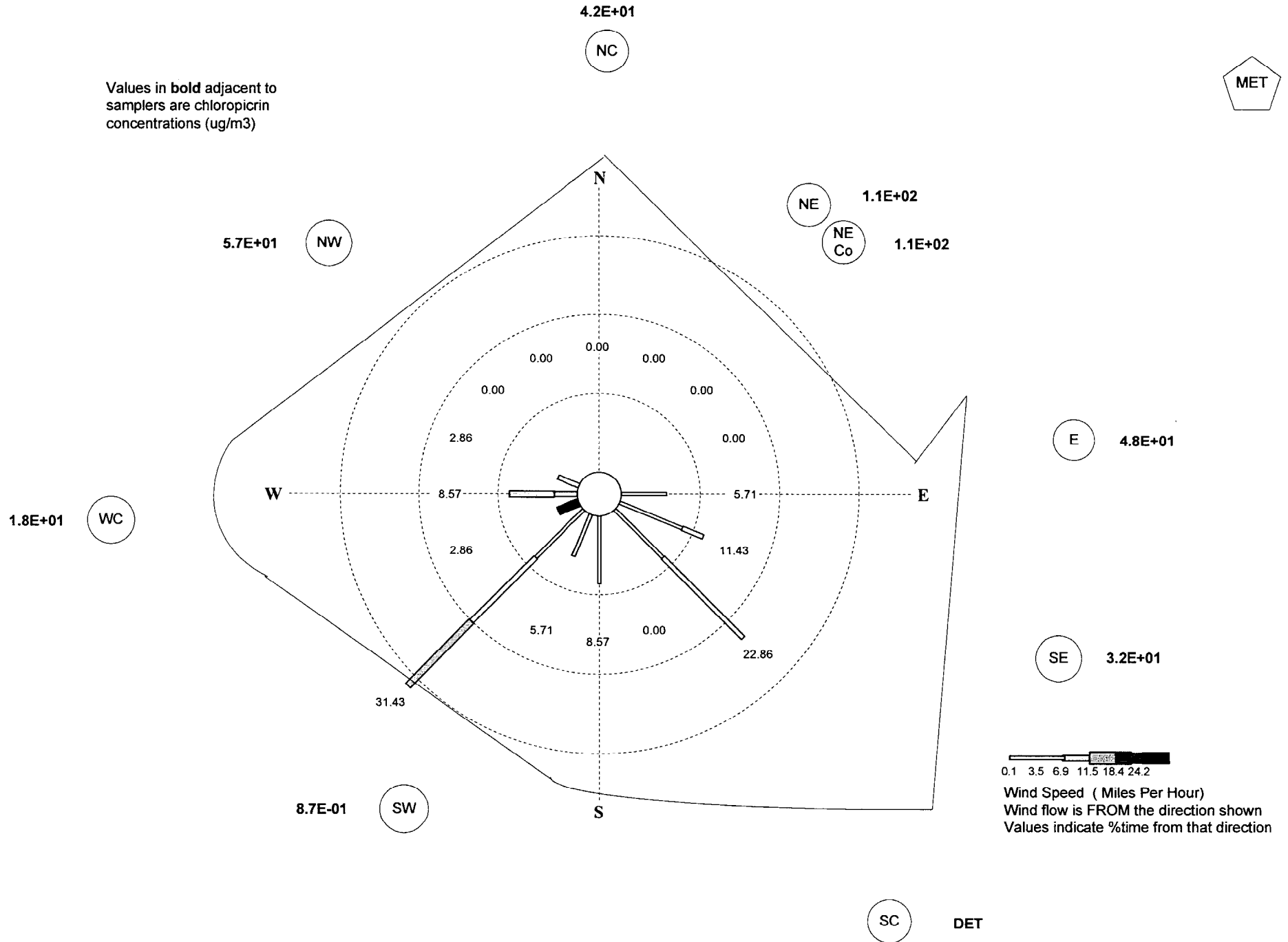


Figure 9  
Period 4 11/14/03 Overnight Chloropicrin (ug/m3)

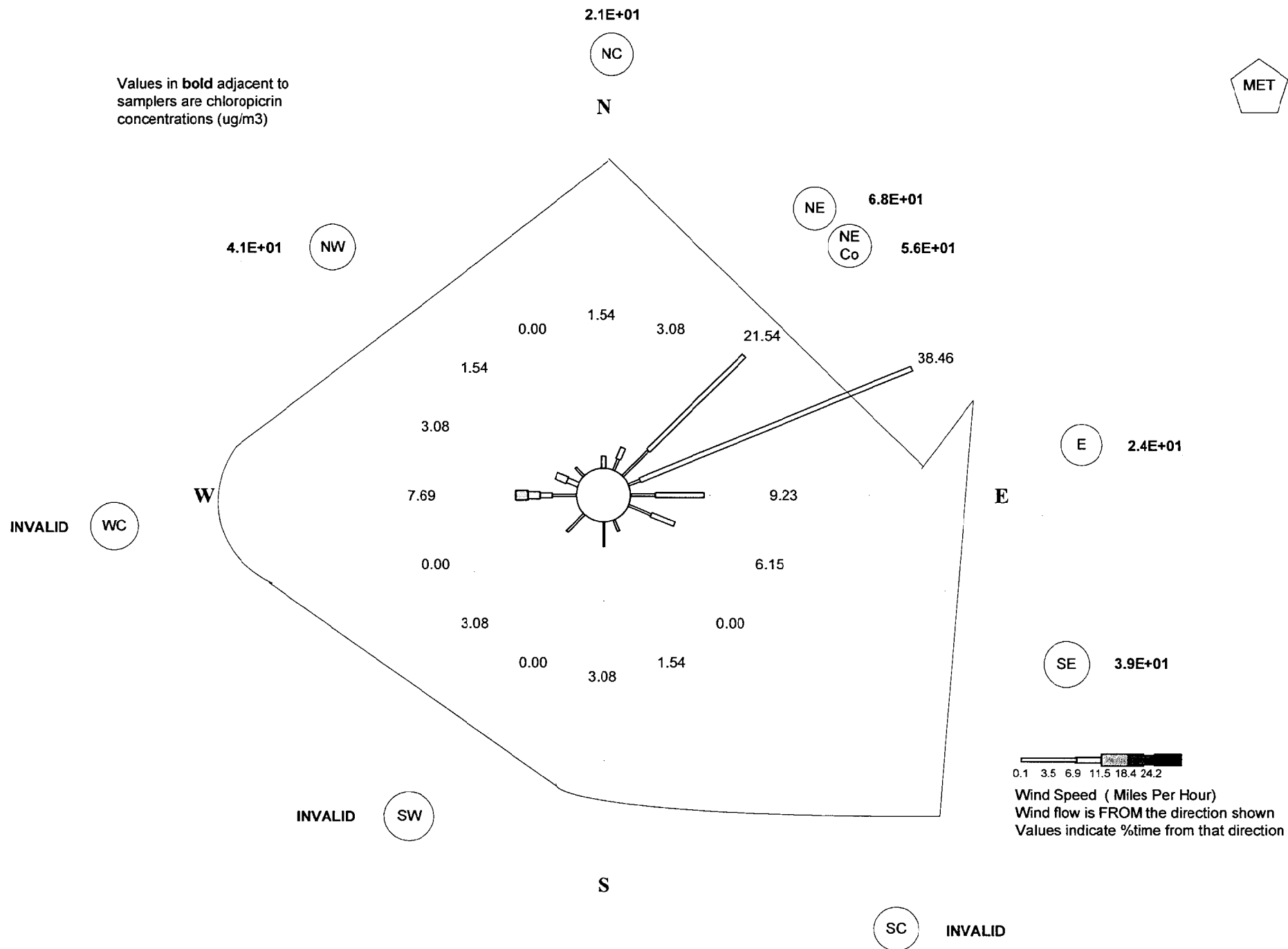


Figure 10  
Period 5 11/15/03 Daytime Chloropicrin (ug/m3)

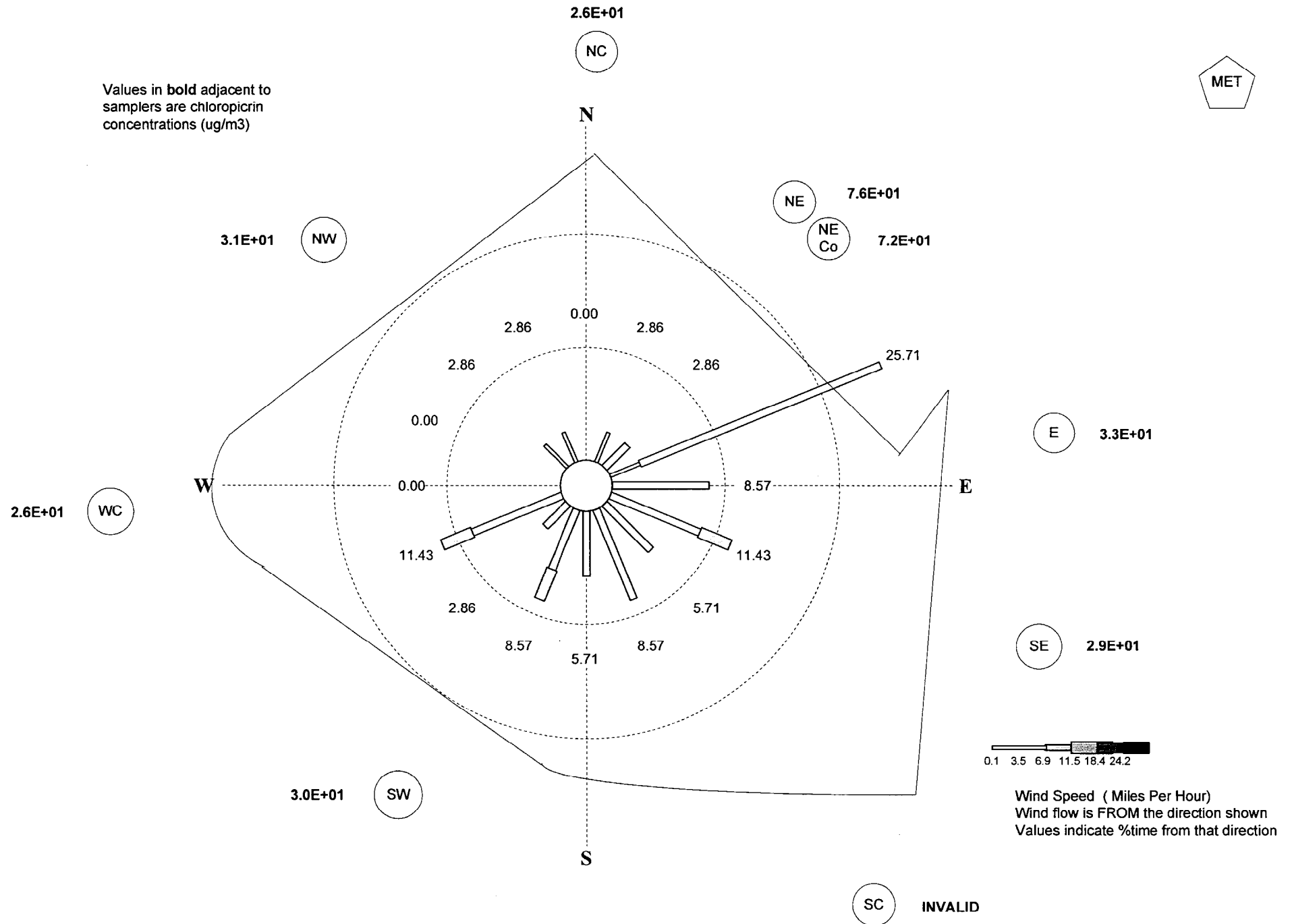
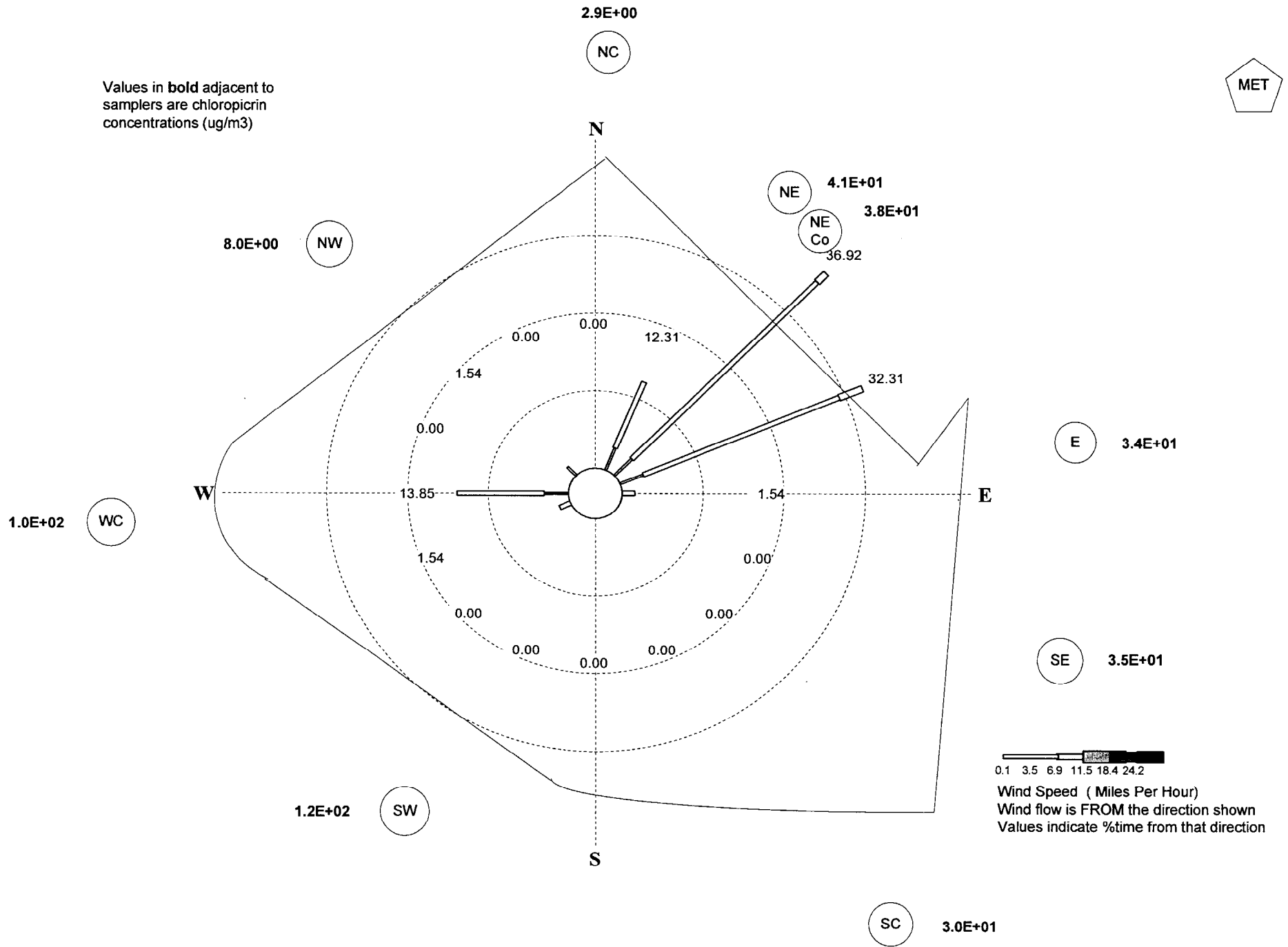


Figure 11  
Period 6 11/15/03 Overnight Chloropicrin (ug/m3)



**Table 6 Site Summary of Chloropicrin Application Monitoring Results (ug/m<sup>3</sup>)**

Sampling Period	NC	NE	E	SE	SC	SW	WC	NW
Background 1		2.7E+02		2.3E+02		1.2E+01		5.8E+00
Background 2		2.1E+02		1.1E+02		2.1E+01		NA
1	2.3E+01	7.1E+01	4.2E+01	6.9E+01	2.6E+00	1.7E+00	1.6E+00	3.8E+00
2	4.8E+01	1.1E+02	9.1E+01	1.5E+02	8.1E+01	1.7E+01	5.5E+01	1.4E+02
3	4.2E+01	1.1E+02	4.8E+01	3.2E+01	Det	8.7E-01	1.8E+01	5.7E+01
4	2.1E+01	6.8E+01	2.4E+01	3.9E+01	NA	NA	NA	4.1E+01
5	2.6E+01	7.6E+01	3.3E+01	2.9E+01	NA	3.0E+01	2.6E+01	3.1E+01
6	2.9E+00	4.1E+01	3.4E+01	3.5E+01	3.0E+01	1.2E+02	1.0E+02	8.0E+00
Maximum	4.8E+01	2.7E+02	9.1E+01	2.3E+02	8.1E+01	1.2E+02	1.0E+02	1.4E+02
Average	2.7E+01	8.0E+01	4.5E+01	5.8E+01	2.8E+01	3.3E+01	4.1E+01	4.7E+01
# Samples	6	8	6	8	4	7	5	7
# >EQL	6	8	6	8	3	7	5	7
# Det	0	0	0	0	1	0	0	0
# <MDL	0	0	0	0	0	0	0	0

Only the higher value of each collocated pair was used to calculate the above statistics.

"Det" results were factored into the average as  $(MDL+EQL)/2 = 0.084 \text{ ug/m}^3$ .

## VI. Field Quality Assurance

Field quality assurance for the application monitoring included the following:

- 1) Four field spikes obtained by sampling ambient air at the application monitoring site. The field spikes were obtained by sampling ambient air during the background monitoring (i.e., collocated with a background sample at the same environmental and experimental conditions).
- 2) One trip spike prepared at the same level as the field spikes. The trip spike was labeled, recorded on the field log-sheet, and transported along with the field spikes and application samples.
- 3) Six lab spikes prepared at the same level as the field and trip spikes. The lab spikes remained in the laboratory freezer and were extracted and analyzed along with the field and trip spikes.
- 4) Collocated (replicate) samples taken for all sampling periods (except the background period) at one sampling location (NE).
- 5) A trip blank was obtained, labeled, recorded on the field log-sheet, and transported along with the field spikes and application samples.

## VII. Quality Assurance Results

### A. Method Development

Refer to Appendix VI (page 102 of the Appendices) for raw data for the MDL determination, for the sample collection and extraction efficiency, and for the storage stability studies. The freezer storage stability study results (page 110 of Appendices) show that chloropicrin is stable for at least 4 weeks. All of the application samples were analyzed within 4 weeks.

### B. Trip Blanks

The application trip blank result was <MDL for chloropicrin.

### C. Application Background Sample Results

Four samples were collected for each of the two background periods from the northeast (NE), northwest (NW), southeast (SE) and southwest (SW) sites. In all cases the results were above the EQL with the highest concentration of 270 ug/m<sup>3</sup> found at the northeast site during "Background 1".

### D. Collocated Sample Results

Six collocated pairs of samples for the application study had both results above the EQL. The relative percent differences (RPD) of the valid data pairs ranged from 4.4% to 19%.

RPD is calculated as:  $\frac{|C1-C2|}{(C1+C2)/2} \times 100$

**Table 7 Collocated Sampler Results**

Sample ID	Chloropicrin (ug/m3)	Average	Relative % Difference
NE-C-1	7.14E+01	6.99E+01	4.4
NE-C-1C	6.83E+01		
NE-C-2	1.09E+02	1.02E+02	14
NE-C-2C	9.44E+01		
NE-C-3	1.13E+02	1.11E+02	4.6
NE-C-3C	1.08E+02		
NE-C-4	6.78E+01	6.18E+01	19
NE-C-4C	5.59E+01		
NE-C-5	7.58E+01	7.40E+01	4.9
NE-C-5C	7.22E+01		
NE-C-6	4.05E+01	3.93E+01	6.0
NE-C-6C	3.82E+01		
AVE=			8.9

## E. Laboratory, Trip and Field Spikes

Laboratory, trip and field spikes were all prepared at the same time and at the same concentration. The spikes are typically prepared in replicate sets of four (4) to allow statistics to be applied if necessary to evaluate differences in the results of three of the sets. Although the protocol specified that four trip spikes were to be prepared, the laboratory prepared only one trip spike for this study. Two additional laboratory spikes were prepared and analyzed for this study for a total of six. The laboratory spikes were placed immediately in a freezer and kept there until extraction and analysis. The trip spike was kept in a freezer until transported to the field. The trip spike sample was kept on dry ice in an ice chest (the same one used for samples) during transport to and from the field and at all times while in the field, except for trip spike sample log-in and labeling.

The field spikes were kept in a freezer until transported to the field. The field spike samples were kept on dry ice in an ice chest (the same one used for samples) during transport to and from the field and at all times while in the field except for the sampling period. Field spikes were collected at the same environmental and experimental conditions as those occurring at the time of ambient sampling. The field spikes were obtained by sampling ambient air through the previously spiked cartridges and were colocated with a background sample. The extraction and analysis of laboratory, trip and field spikes normally occurs at the same time. Special Analysis Section staff prepared laboratory, trip spikes and field spikes for the application monitoring.

- 1) Laboratory Spikes: The laboratory spike results for the application study are listed in Table 8. Each of the spike cartridges was spiked with 100 ng of chloropicrin. The average recovery for chloropicrin for the application lab spikes was 96%.

**Table 8 Chloropicrin Laboratory Spike Results**

Sample ID	Chloropicrin Amount (ng)	Expected Amount (ng)	Percent Recovery
LS01	94.41	100	94%
LS02	87.12	100	87%
LS03	102.66	100	103%
LS04	107.61	100	108%
LS05	89.40	100	89%
LS06	92.73	100	93%
Ave.=			96%

- 2) Trip Spike: The trip spike result for the application study is listed in Table 9. One cartridge was spiked with 100 ng of chloropicrin and had recovery for chloropicrin of 104%. This result is consistent with the lab spike results and indicatea that the sample transport, storage and analytical procedures used in this study produce acceptable results for chloropicrin.

**Table 9 Chloropicrin Trip Spike Result**

Sample ID	Chloropicrin Amount (ng)	Expected Amount (ng)	Percent Recovery
C-TS	103.62	100	104%

- 3) Field Spikes: The field spike results for the application study are listed in Table 10. Each of the cartridges was spiked with 100 ng of chloropicrin. As reported by the laboratory, the average recovery for chloropicrin for the application field spikes was 91%. However, the spike amounts were inappropriate relative to the background levels in the samples for those collected by the southeast and northeast samplers. The high levels in those samplers were most likely due to the prevailing winds and the residual from applications done adjacent to the site only two days before. The southwest and northwest samplers did not receive the same impact and may be considered valid. However, even for the southwest and northwest samples, the spike levels are still low relative to the background levels. Although there is no strict criteria established, in general, it is desirable to have the spike level at least five times higher than the background levels (i.e., background level  $\leq$  20% of spike level). Thus, caution should be used in evaluating the field spike results.

**Table 10 Chloropicrin Field Spike Results**

Sample ID	Chloropicrin Amount (ng)	Background* Amount (ng)	Corrected Amount (ng)	Expected Amount (ng)	Percent Recovery
SE-C-B1-FS	14769.00	11037.00	NA	100	NA
SW-C-B1-FS	826.50	730.95	95.55	100	96%
NW-C-B1-FS	476.62	390.76	85.86	100	86%
NE-C-B1-FS	15331.00	17298.00	NA	100	NA
Ave.=					91%

\*Amount of chloropicrin found in the collocated background sample.

NA - invalid spike